Enhanced Light–Matter Interactions in Self-Assembled Plasmonic Nanoparticles on 2D Semiconductors

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1. Introduction

2D semiconductors with atomic layer thicknesses provide numerous material categories for unexplored physics and applications.[1–3] Monolayer platforms of transition-metal dichalcogenides (TMDs) fabricated via mechanical exfoliation or chemical vapor deposition (CVD)[4] have attracted considerable interest for high-performance optoelectronics.[5] The reduced dielectric screening in monolayer TMDs allows for tightly bound excitons and strong light–matter interactions.[6] Numerous applications at ultrathin thicknesses, including lasing,[7] optical communications,[8,9] photodiodes,[10,11] and light-emitting diodes,[12] have been demonstrated owing to the outstanding optical properties of TMDs. Nevertheless, their light-emission performances for practical applications are limited by their weak absolute absorption and low quantum efficiency at the nanoscale thickness. For improving the light–matter interactions in quantum emitters and various optoelectronics, hybridization with plasmonic structures has been widely investigated.[13,14] Hybridization of metallic nanostructures for localized surface plasmon resonance (LSPR) and the propagation of surface plasmon polaritons provides significant enhancement of the light–matter interactions in monolayer TMDs.[15–19] The local field enhancement and Purcell effect near the plasmonic nanostructures promote the light absorption and emission in 2D materials.

For integrating plasmonic nanostructures with TMDs, lithography patterning,[16,19–21] nanostructure decoration,[17,18] and nanoparticle (NP) self-assembly methods[24,25] are widely used. Various nanostructures fabricated via e-beam lithography patterning have good fabrication controllability for tuning the LSPR resonance frequency; however, downsizing to sub-100 nm dimensions is challenging.[16,20–22] The utilization of chemically synthesized Au or Ag nanostructures, including particles, cubes, and wires is another route for plasmonic hybridization. While the sub-50 nm dimensions of such nanostructures are beneficial for examining the local properties beyond the scaling limit of e-beam lithography, homogeneous decoration over micrometer ranges is difficult owing to the colloidal agglomeration.

The self-assembly processes to form NPs are utilized as one alternative platform for small-dimension and large-area hybridizations.[24,25] In metal film deposition, adatoms on the substrates are clustered in an island growth mode below a
nominal thickness of \( \approx 10 \text{ nm} \). The NP sizes are manipulated by changing the deposition thickness, surface modification of substrates, thermal annealing. While strong localization of the electromagnetic waves between NPs allows the photoluminescence (PL) enhancement to reach a factor of \( \approx 15 \), the interspacing and density control of NPs remain challenging. One exceptional self-assembly method, which was developed for visualizing the macroscopic defect distribution of TMDs, involves anchoring Ag ion clusters on CVD-grown TMDs. The clustered Ag-NPs on TiO\(_2\)-covered Ag substrates prepared via thermal annealing are anchored on defect sites of TMDs via a photochemical reaction in an aqueous solution under light illumination, where the Ag clusters \( \approx 200 \text{ nm} \) in diameter exchange charges with TMD point defects with the assistance of light. While the point defect distributions of monolayer TMDs were simply visualized using dark-field (DF) optical microscopy (OM) owing to the LSPR of the anchored Ag-NPs, the benefits of the plasmonic hybrids as quantum emitters were not systematically studied.

Here, we propose a method for decorating the Ag-NPs on native defect sites of TMD monolayers, where such Ag-NPs were self-assembled via dry aging without thermal annealing. This was implemented by transferring MoS\(_2\) layers onto Ag films with a thin dielectric spacer, followed by aging in a vacuum desiccator at room temperature. Moreover, we systematically studied the prominently improved light–matter interactions in the TMD/Ag-NP hybrids. The PL intensity of MoS\(_2\) on the Ag-NPs was enhanced up to 35-fold compared with bare MoS\(_2\) owing to the strong local field enhancement and strain-texturing effects near the plasmonic NPs. The LSPR effects of this hybrid were investigated via numerical simulations and surface characterizations.

### 2. Results and Discussion

Figure 1a presents perspective (top) and cross-sectional (bottom) views of the layered sample structures before and after aging. To obtain ultrasmooth surfaces, Ag films (100 nm) were deposited on the Si wafer and peeled off using an epoxy adhesive layer and polyethylene terephthalate (PET) substrates, which is known as the peeling-off technique. A spacer layer of SiO\(_2\) (10 nm) was deposited on the smooth Ag surface, and a then poly(methyl methacrylate) (PMMA)-coated CVD-MoS\(_2\) layer was transferred onto the top of the SiO\(_2\)/Ag/epoxy/PET-substrate in deionized (DI) water, which is known as the wet transfer method. For the aging process, this sample was stored in a vacuum desiccator at room temperature for 17 d. The detail sample fabrication processes are described in the Experimental Section and Figure S1a in the Supporting Information. The detail progress of the Ag-NP evolution during aging is visualized in Figure S1b in the Supporting Information.
Figure 1b shows bright-field (BF, top) and DF (bottom) OM images of the sample before and after aging. Notably, after aging, black dots are clearly observed only at the MoS_2 flake region in the BF image compared with the as-transferred state. Such contrast between states is prominent in DF images. Bright spots are only observed in the MoS_2 region in the after-aging state, whereas no contrast is visualized in the as-transferred state. We attribute this bright light scattering in the DF mode to the light scattering of LSPR near Ag-NPs. The morphologies of the Ag-NPs were visualized via scanning electron microscopy (SEM) and atomic force microscopy (AFM), as shown in Figure 1c,d, respectively. NP islands ≈20–60 nm in height were formed in the MoS_2 flake regions, which was far more prominent at the flake edges. The average Ag-NP diameter was estimated to be ≈50 nm (also see Note S1, Supporting Information).

Figure 2a,b shows comparative images of the BF, DF, and PL mapping for the same sample area. The bright parts between the DF image and PL mapping image correspond to each other, while a uniform PL intensity distribution was observed in the reference MoS_2 sample (Ref-MoS_2) on SiO_2/Si substrates (see Figure S2 in the Supporting Information). Figure 2c shows selected spectra for Ref-MoS_2 as well as the Off-NP and On-NP regions (MoS_2 on SiO_2/Ag/epoxy/PET substrate) of Figure 2b. While the PL intensities for Off-NP and Ref-MoS_2 are of similar order, that for On-NP is ≈35-fold higher than others, which is attributed to the improved light–matter interaction caused by plasmonic effects near Ag-NPs. Compared with other plasmonic hybrids, the order of magnitude of this PL enhancement is comparable [16,23,25] or significantly higher [18], except for a hybrid based on the metal–insulator–metal gap mode [17,19]. Similarly, by using 633 nm laser excitation, the PL intensity enhancement reaches ≈15-fold for On-NP compared to Ref-MoS_2 (see Figure S3 in the Supporting Information). By using the Ag-NP-occupied area measured via AFM and SEM (see Note S1 in the Supporting Information), an effective PL enhancement factor (EF) was estimated to be up to enhancement factor 800 by using the formula [19]

$$EF = \frac{I_{On-NP}}{I_{Ref}} \times \frac{A_{on}}{A_{ag-NP}}$$  

Figure 2. PL and Raman spectroscopy characteristics of MoS_2/Ag-NP hybrids and bare MoS_2. a) OM images of the BF (left) and DF (right) modes and b) PL intensity map of MoS_2/Ag-NP hybrids. c) Representative PL spectra for Ref-MoS_2 (MoS_2 on an SiO_2/Si wafer), as well as the Off-NP (dark region) and On-NP (bright region) of panel (b). An arrow indicating the 35-fold enhancement of the PL intensity for On-NP compared with Ref-MoS_2. Inset: A-exciton peak position for each PL spectrum. d) Schematic representation for strained MoS_2 due to Ag-NP formation. e) Representative Raman spectra for Ref-MoS_2, Off-NP, and On-NP. f) Raman peak positions of the A_{1g} and E_{2g} modes for each spectrum.
where \( I_{\text{On-NP}} \) and \( I_{\text{Ref}} \) are the PL intensities for On-NP and Ref-MoS\(_2\), respectively, \( A_{\text{spot}} \) is the laser spot, and \( A_{\text{Ag-NP}} \) is the Ag-NP coverage area in Figure 2c.

The inset of Figure 2c shows A-exciton peak positions for each spectrum. The A-peak for Off-NP (=1.845 eV) and On-NP (=1.827) are redshifted from that of Ref-MoS\(_2\) (=1.855 eV). It is known that a deformation and strain in monolayer MoS\(_2\) transferred onto SiO\(_2\)-nanocone-patterned substrates allows a strain-induced exciton energy reduction. Grooved shapes of artificial patterns generate the least and most strained regions in MoS\(_2\) layers, resulting in strain-textured 2D crystals. This concept is depicted for our MoS\(_2\)/Ag-NP hybrids in Figure 2d, where the less-strained regions are not clearly defined, because the spatial resolution (=500 nm) of the PL mapping image is larger than the mean Ag-NP size (=50 nm) and the interparticle distances are irregular (Figure 1c). Nevertheless, we defined the Off-NP regions as the less-strained regions. While the overall PL peak redshift for Off-NP reached ≈10 meV\([28]\) in the On-NP region with strong PL enhancement, the peak redshift (=30 meV) was far more prominent, which is ascribed to the maximum tensile-strain effect at the most strained region on Ag-NPs\([28]\) and doping effects induced by plasmonic hot electrons of the metallic NPs\([29]\). Moreover, in the modulated band gaps of strain-textured MoS\(_2\), photogenerated excitons funneling from larger band gap regions into smaller band gap regions. As a result, the PL intensity enhancement and PL peak redshift at the most strained region are allowed in comparison to the less strained regions\([28]\). Therefore, the strain effect of Ag-NPs resulting in strain-induced exciton funneling possibly affects the PL intensity enhancement and PL peak shift for On-NP, as indicated in Figure 2c. The plasmonic and strain effects imposed by Ag-NPs are also investigated via the Raman peak shifts. Figure 2e shows representative Raman spectra for Off-NP and On-NP compared with Ref-MoS\(_2\). While the peak intensity for Off-NP is comparable to that of Ref-MoS\(_2\), that for On-NP is increased by ≈10 times, which is ascribed to the local field enhancement effects near plasmonic NPs\([23,30,31]\) agreeing well with the prominently increased PL intensity in Figure 2c. Moreover, the \( E_{1g} \) and 2LA(M) modes are dramatically enhanced for On-NP, which is a typical phenomenon in plasmonic hybrids based on monolayer TMDs\([30,31]\). The \( E_{1g} \) mode (=278 cm\(^{-1}\), in-plane mode) is inactive in the backscattering geometry on a basal plane owing to Raman selection rules\([30]\). However, the presence of the \( E_{1g} \) peak indicates an intense tensile strain arising from Ag-NPs, as also observed in the \( E_{2g} \) mode. Figure 2f summarizes the Raman peak position changes. In On-NP, while the redshift of the \( A_{1g} \) mode related to the doping effect is not prominent, the peak redshift of the \( E_{2g} \) mode reaches ≈8 cm\(^{-1}\) from the \( A_{1g} \) (=404.5 cm\(^{-1}\), out-of-plane mode) and \( E_{2g} \) (=387.5 cm\(^{-1}\), in-plane mode) peaks of Ref-MoS\(_2\). We attribute this large \( E_{2g} \) redshift to a tensile-strain effect, because Raman splitting of \( E_{2g} \) at ≈8 cm\(^{-1}\) was observed in Ag-NP deposited MoS\(_2\) monolayers owing to the effective tensile strain of ≈2\%\([28,32,33]\).

**Figure 3** shows a schematic representation of DF scattering under grazing light incidence on MoS\(_2\)/Ag-NP hybrids. To investigate the LSPR modes, spectrum and mapping images for the DF scattering were measured using a lab-made...
optical microscope equipped with a DF lens (X 100, 0.9 NA). Figure 3b shows a DF scattering mapping image and an OM image (inset) of the sample. Strong contrasts due to light scattering at the plasmonic nanostructures are observed inside the MoS\(_2\) flakes, while this contrast is negligible outside of the flakes, agreeing well with the DF mode OM images in Figures 1b and 2a. Figure 3c shows the average spectrum (top) inside MoS\(_2\) flakes and a single point spectrum (bottom) at a position P, as indicated in Figure 3b. Although the peak shapes of the spectra are broad owing to the irregular distribution in the size and shape of Ag-NPs, as shown in Figure 1c,d, two main peaks are clearly observed in both spectra, which are indexed to \(\alpha\) (500–600 nm) and \(\beta\) (620–700 nm), respectively. To identify these two plasmonic modes, finite-difference time-domain (FDTD) simulations were conducted using DF scattering simulation methods.\(^{[34]}\) Figure 3d depicts a simulation geometry for Ag-NP/MoS\(_2\) hybrids, where \(D\) is the NP diameter. We assume that the ultrathin monolayer semiconductors are negligible for DF scattering and the NP structure is a sphere for simplified simulations.\(^{[14]}\) Figure 3e depicts a simulation geometry for Ag-NP/MoS\(_2\) hybrids, where \(D\) is the NP diameter. We assume that the ultrathin monolayer semiconductors are negligible for DF scattering and the NP structure is a sphere for simplified simulations.\(^{[14]}\) Figure 3f shows the scattering spectrum for \(D = 50\) nm (selected from Figure 3e). Although the simulation spectrum slightly blueshifts, the calculated peak ranges of \(\alpha\) (500–550 nm) and \(\beta\) (600–700 nm) quantitatively agree with the experimental result for the single point spectrum (bottom) in Figure 3c. The inset images in Figure 3f show the calculated electric-field (\(E\)) distribution maps near Ag-NPs, where an out-of-plane direction of the electric field was considered for the \(\alpha\) and \(\beta\) modes, respectively. The plus/minus signs in the scale bar indicate the polarity of the optical electric field. Two different plasmonic resonant modes are generated near Ag-NPs: a symmetric resonance mode for the \(\alpha\) peak and an asymmetric resonance mode for the \(\beta\) peak. The electric field is strongly confined not only at a dielectric gap but also around Ag-NPs. Therefore, the plasmonic resonance near Ag-NPs is attributed to the PL enhancement of the MoS\(_2\) layer on top of Ag-NPs. Notably, the \(\alpha\) and \(\beta\) peak positions correspond to the excitation laser wavelength (514 nm) and the A-exciton peak position (660–680 nm).

This study raises the question of whether our process is generally applicable for other TMDs. We conducted the same hybridization process for CVD-grown triangular WS\(_2\) monolayers, and the results are shown in Figure 4a. While no contrast was observed in DF mode of OM images for a zero-day-aging sample, Ag-NPs start to be found around flake boundaries after 2 d of aging. After 8 d of aging, the Ag-NPs were fully observed inside of WS\(_2\) flakes, which is similar to the case of MoS\(_2\) (see detail in Figure S4 in the Supporting Information). Meanwhile, the Ag-NP density and formation
speed in WS\textsubscript{2} is dissimilar to those in MoS\textsubscript{2}, which is attributed to difference in chalcogen vacancy densities between WS\textsubscript{2} and MoS\textsubscript{2}. Native defects such as chalcogen vacancies are crucial for decorating Ag-NP to CVD-grown TMDs in the conventional Ag-NP hybridization method based on photochemical reactions, where dissimilar Ag-NP densities were visualized in various CVD-grown TMD monolayers because of different defect distributions for each TMD.\cite{26}

To elucidate an effect of chalcogen vacancy distribution for Ag-NP generation, we conducted Ag-NP self-assembling process for hexagonal (h-) WS\textsubscript{2} monolayers. The flake shapes and native defects of CVD-grown WS\textsubscript{2} depend on growth conditions. Under a high flow rate of carrier gas, a growth mode of WS\textsubscript{2} monolayers changes from triangular to hexagonal shapes. As a result, the monolayer h-WS\textsubscript{2} consists of two alternating defect domains, i.e., S-vacancy (SV)-rich and W-vacancy (WV)-rich domains. Using such h-WS\textsubscript{2}, therefore, a clear contrast owing to the density effect of chalcogen vacancy can be visualized in Ag-NP self-assembling process. Figure 4b shows BF and DF modes of OM image for the as-transferred (top, i and ii) and after-aging (bottom, iii and iv) states of h-WS\textsubscript{2}. While the as-transferred state exhibits hexagonal shape of flake in BF mode and a negligible scattering contrast in DF mode (Figure 4b-i and ii), a clear optical contrast resulting from Ag-NP generation is visualized in each mode for after-aging state (Figure 4b-iii and iv). Moreover, the optical contrast distinguishes alternating domains, i.e., high Ag-NP density in SV and low Ag-NP density in WV. Each domain is determined via PL mapping for as-transferred state of h-WS\textsubscript{2} shown in Figure 4c-i, where PL intensity for SV domain is two orders of magnitude higher than that for WV domain.\cite{37}

Meanwhile, such a PL intensity contrast for heterogeneous domains of h-WS\textsubscript{2} is inverted after aging. Notably, PL intensity of SV is near three times reduced than that of WV as shown in Figure 4c-ii for after-aging state, which is ascribed to the dominant charge-quenching effect of WS\textsubscript{2} on Ag-NPs for high quantum yield materials. In contrast to low quantum yield materials such as MoS\textsubscript{2}, WS\textsubscript{2} with a high quantum yield is strongly affected by charge quenching at metal contacts.\cite{25} We confirm that the PL intensity of triangular WS\textsubscript{2} is ≈15 times higher than that of triangular MoS\textsubscript{2} (see Figure S5 in the Supporting Information). Therefore, PL intensity for MoS\textsubscript{2} enhances owing to the Ag-NP self-assembling but that for WS\textsubscript{2} rather reduces. Moreover, the PL quenching effect is more dominant for SV than WV, because Ag-NP densities are prominently different between domains; Ag-NPs at WV domain are much reduced owing to a lack of SV in comparison to high-density Ag-NPs at SV domain. Figure 4d shows comparative PL spectra of as-transferred and after-aging states for SV and WV domains, respectively, where each spectrum is an average value of the corresponding domain region. For after-aging state, while the PL intensity reduction for WV is near two times, that for SV reaches three orders of magnitude, compared to as-transferred state. Thus, overall PL intensity for SV is rather reduced than that for WV, resulting in an inverted PL intensity contrast of each defect domain between as-transferred and after-aging states, as shown in Figure 4c. In contrast to MoS\textsubscript{2}, average PL peak positions of after-aging state blueshift for both WV and SV, which is ascribed to a net effect of complicated strain texture, Ag-NP size distribution, doping, and charge quenching, etc. in WS\textsubscript{2}/Ag-NP hybrids.

We propose a self-assembly Ag-NP formation mechanism based on the experimental results. Figure 5 depicts a possible process of Ag-NP clustering. i) The PMMA/CVD-TMD layers were transferred onto SiO\textsubscript{2} (10 nm)/Ag (100 nm)/epoxy/PET-substrates in DI water. Here, the PMMA cover layer and the flexible PET substrate are main factors for the Ag-NP self-assembly process. The Ag-NP distribution density and generation speed are drastically reduced in cases without the PMMA cover layer (see Figure S6 in the Supporting Information). Because water and moisture promote the mobility of Ag atoms for clustering,\cite{35} the PMMA cover layers sustaining such a wet condition between the MoS\textsubscript{2} layer and SiO\textsubscript{2} interface may
allow the promotion of Ag-NP self-assembly. The lateral strain effect of flexible Ag/epoxy/PET-substrates is not negligible in this Ag-NP formation, because the Ag-NP self-assembly process was also drastically retarded on rigid SiO₂/Si wafer substrates (see Figure S7 in the Supporting Information).

Based on these possible formation is preferred at MoS₂ flake edges and grain boundary sites of MoS₂ reduces the adsorption energy, [26] which atoms that diffuse to the SiO₂/MoS₂ interfaces are adsorbed in this Ag-NP formation, because the Ag-NP self-assembly effect of flexible Ag/epoxy/PET-substrates is not negligible. The lateral strain regime via surface diffusion even at room temperature. [39] allows for pseudoelastic diffusion of Ag atoms at sub-10 nm over, the accumulated stress in substrates is greater for the flexible substrates than for the rigid substrate, as discussed above. One possible pathway for relaxing the accumulated compressive stress is atom diffusion in metal films. [38] In addition, either external force or capillary energy minimization allows for pseudoelastic diffusion of Ag atoms at sub-10 nm regime via surface diffusion even at room temperature. [19] Thus, we consider the film stress as another reason for the Ag diffusion through the SiO₂ spacer in addition to a porous structure of SiO₂ for capillary effect. Based on these possible mechanisms, the heat treatment is another way to modulate the clustering speed and size of Ag-NPs. Because the thermal annealing which generally improves the atomic diffusions by increasing the atomic mobility, the Ag diffusion and self-assembling process of Ag-NPs can be accelerated. However, the heating effect can accompany unwanted side effects including adhesion problems at interfaces, strain effect, bubbling effect, and so on. ii) Self-assembled Ag-NP was formed via Ag atom clustering under MoS₂ layers. As previously discussed, the Ag atoms that diffuse to the SiO₂/MoS₂ interfaces are adsorbed on the defect sites of MoS₂, minimizing the adsorption energy, and the Ag clustering evolves over time. The defect sites of MoS₂ appear to be crucial in this process, because the Ag-NP formation is preferred at MoS₂ flake edges and grain boundaries or line defects, which are more defective than the inside of flakes, as observed in Figures S1 and S4 in the Supporting Information. Notably, our hybridization process differs from Ag-cluster decoration on TMDs for visualizing point defects based on a photochemical reaction between TiO₂ and Ag. Most importantly, our process does not involve thermal annealing, whereas thermal annealing is essential process for generating large Ag clusters with ≈200 nm-diameter in the previous method. [35] In summary, we demonstrated a method for hybridizing Ag-NPs onto CVD-grown TMD multilayers via self-assembly. In contrast to conventional self-assembly methods based on thermal annealing and photochemical reactions, for PMMA/CVD-MoS₂ layers on SiO₂ (10 nm)/Ag (100 nm)/epoxy/PET-substrates, we observed self-clustering of Ag-NPs on MoS₂ defect sites via a few days of aging in vacuum desiccators at room temperature. The self-diffusion of Ag atoms from Ag films to MoS₂ layers through a thin and porous SiO₂ spacer resulted in the self-assembly of Ag-NPs (>50 nm diameter) on MoS₂ defect sites without thermal treatment or light illumination. The PL and Raman intensities of On-NP were increased, and their peak positions were redshifted compared with bare MoS₂. The PL enhancement for On-NP compared the bare MoS₂ reached ≈35-fold (estimated <EF> ≈ 800). While the LSPR of self-clustered Ag-NPs allows for enhancing the local optical fields and improving the light–matter interactions of the MoS₂ layers, strain and doping effects due to the Ag-NP formation at the bottom of the MoS₂ layers result in PL and Raman peak shifts of MoS₂. The plasmonic resonance modes of these hybrids were calculated via FDTD simulations. The two dominant resonance modes (symmetric and asymmetric) corresponded to DF scattering spectra for On-NP, and the resonance peak positions agreed with the excitation laser wavelength and the A-exciton position of MoS₂. This hybridization method was generalized using CVD-grown WS₂ monolayers as well. Our studies pave the way to manipulate the self-assembly process of plasmonic hybrids for 2D semiconductors.

3. Experimental Section

Substrate Preparation: An Ag film (100 nm) was deposited on a Si substrate via thermal evaporation. This Ag film was detached from the Si substrate via a peel-off technique. [27] For the peel-off process, 1 g of an epoxy chemical (KUKDO Chemical, type YDF-175) and 1 g of a hardener chemical (KUKDO Chemical, type 0331) were mixed together and placed in a vacuum chamber for 30 min to remove bubbles during mixing. Next, the mixture was dropped onto PET substrates on a hot plate of 55 °C. The epoxy became soft and spread over the PET surface. Sequentially, the Ag/Si substrate was attached to the soft epoxy and pressed slightly to remove the trapped bubbles between the surfaces of the epoxy and substrate. To harden the epoxy layer, the sample was cured at 55 °C for several hours. Owing to the weak adhesion between the surfaces of Si and Ag, the Si substrate was detached from the Ag/epoxy/PET substrates. A SiO₂ dielectric spacer (10 nm) was deposited on the detached Ag/epoxy/PET substrate via an e-beam evaporation method. The MoS₂ and WS₂ monolayer flakes were synthesized on a SiO₂ (300 nm)/Si substrate using CVD methods. [40] The synthesized monolayers were transferred onto the SiO₂ spacer-deposited Ag/epoxy/PET substrates via the PMMA supporting method in DI water and dried. The PMMA/TMD film transferred samples were stored in a vacuum desiccator for aging. After the clustering of the Ag particles, the PMMA layer was removed by dipping the sample in acetone for optical characterization.

Characterization: The topography and morphology of samples were examined using AFM (Nano Navi) in the tapping mode, as well as SEM (JEOL JSM7000F). Optical microscopic images for the BF and DF modes were obtained using an optical microscope (0.9 NA, ZEISS, Axio Imager 2). Spectrum and mapping images for plasmonic DF scattering were obtained using a lab-made optical microscope equipped with a DF lens (0.9 NA, Nikon) and a short-pass filter (390 nm). A DF condenser was used to illuminate the samples with an oblique beam. PL and Raman spectra were measured under ambient conditions using a lab-made confocal microscope equipped with an Ar laser (514 nm wavelength) and an objective lens (0.9 NA) as well as commercial confocal Raman imaging system (XperRam200VN, NANOBASE, Inc.). The DF scattering spectra for self-assembled Ag NPs with various diameters were calculated using an FDTD numerical solution.
Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

This work was supported by the Institute for Basic Science of Korea (IBS-R011-D1) and Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (2018R1D1A1A02046206).

Conflict of Interest

The authors declare no conflict of interest.

Keywords

localized surface plasmon resonance, photoluminescence, Raman, self-assembly, silver nanoparticles, transition-metal dichalcogenides

Received: July 26, 2018
Revised: September 18, 2018
Published online: October 10, 2018